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Visible spectra of Cu_2 molecule

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Abstract : Thermal emission spectrum of Cu_2 molecule has been reinvestigated in the visible spectral region $\lambda\lambda$ 4000 – 6000 Å using high temperature graphite tube furnace at a temperature in the vicinity of 2100°C in an atmosphere of argon. A total of 171 bands have been recorded at a reciprocal linear dispersion of 7.3 Å/mm and 3.7 Å/mm and classified into two systems *viz* A – X and B – X. Out of 171 bands observed 100 are new and are nicely explained by the proposed analyses. The analysis is confirmed by the presence of isotope effect for $^{65}Cu^{63}Cu$ and $^{63}Cu^{63}Cu$ in the bands of the A – X system.

Keywords : Thermal emission spectra, spectra of Cu_2 molecule, vibrational analysis, vibrational isotope effect

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1. Introduction

It may be observed that due to the developments of the studies of phenomena such as chemisorption and catalysis where metal clusters play an important role, there has been increasing interest in the electronic structure and electronic properties of small transition metals aggregates.

The band spectrum of Cu_2 molecule has been investigated by several earlier workers [1–13]. The emission spectrum of Cu_2 molecule was first recorded by Kleman and Lindkvist [1] in the spectral region $\lambda\lambda$ 4000 – 6000 Å. They classified the recorded bands into two systems *viz*. A – X and B – X. The vibrational analysis was confirmed by observing the isotope shifts in the system A – X. Aslund *et al* [4], on the basis of the rotational analyses of the (1, 0), (0, 0) and (0, 1) bands of the B – X system, suggested that the B – X system arose from the transition $^1\Sigma_u^+ - {}^1\Sigma_g^+$. Pesic and Weniger [5] reported the rotational structure of the A – X system and assigned A state as $^1\pi_u$. Later Lochet [7] identified only P and R branches from the fluorescence study of the A – X system and reported that A state to be $^1\Sigma_u^+$ instead of $^1\pi_u$. A similar results for the A – X system's transition had been reported in refs. [10] and [11].

A close scrutiny of the available references demonstrates that the analysis of the Kleman and Lindkvist [1] is correct for the A – X system. But the two results reported in

refs. [5] and [7], regarding the transition for the A – X system, differ from each other. On the other hand, for the B – X system, Kleman and Lindkvist [1] have observed only 10 bands and reported that heads are not very marked and are diffused. As a result they were unable to fix the positions of the heads in the higher sequences. In the present investigation we have identified the well defined sequences and have analysed nicely by the proposed analysis. Therefore, the present investigation is carried out with a view to search out more spectroscopic information about the Cu_2 molecule.

2. Experimental

A small quantity of pure substance (copper foil) was inserted into the experimental tube of the graphite furnace (described by Saha *et al* [14]) which was 8 cm long and had an inner diameter 0.8 cm. After making necessary routine adjustments and evacuation of the furnace chamber, argon gas was filled into the furnace at a pressure of 50 cm of mercury in order to reduce the rapid effusion of the vapours from the open end of the graphite tube. The sample was then heated by passing an electrical current through the tube and observation were made at various temperature ranging from 2000°C to 2200°C. Well defined bands in the region $\lambda\lambda$ 4000 – 6000 Å were obtained at a temperature of about 2100°C. A Plane Grating Spectrograph with a grating blazed at λ 5600 Å and total lines ruled 45600 was used to photograph the spectra with the dispersion 7.3 Å/mm and 3.7 Å/mm. ORWO 400 ASA black and white films were used for recording the spectrum in the exposure time from 10 to 18 minutes. A copper dc arc was used for comparison spectrum. The measurements were performed using Abbe Comparator with least count of 0.0001 cm.

3. Results and discussion

Thermal emission spectrum of Cu_2 molecule, shown in Figures 1 and 2, has been recorded in the spectral region $\lambda\lambda$ 4000 – 6000 Å. The spectrum is well developed and almost free from atomic lines of copper. In the stronger sequences, the bands are well resolved and single headed. The authors have recorded about 171 bands and analysed them into the two systems *viz.* A – X and B – X. Out of 171 bands observed 100 band heads have been reported for the first time while rest include the bands reported by Kleman and Lindkvist [1] and later Preuss *et al* [8]. The following are the vibrational analyses proposed by the authors.

3.1. System A – X .

This system was studied for the first time by Kleman and Lindkvist [1] and found to lie in the spectral region $\lambda\lambda$ 4850 – 5750 Å. They analysed the recorded bands into a single system and suggested that the system arose from the ground state. We have recorded the thermal emission spectrum of A – X system and found that the system was extended in lower and higher spectral region. About 112 bands have been recorded and analysed into the Δv = 3 to –10 sequences. The sequences Δv = 3, 2, –9 and –10 have been photographed for the first time. It has been found that the vibrational constants for the ground state are identical as reported by Preuss *et al* [8]. The additional band head data, visual estimates of intensities and

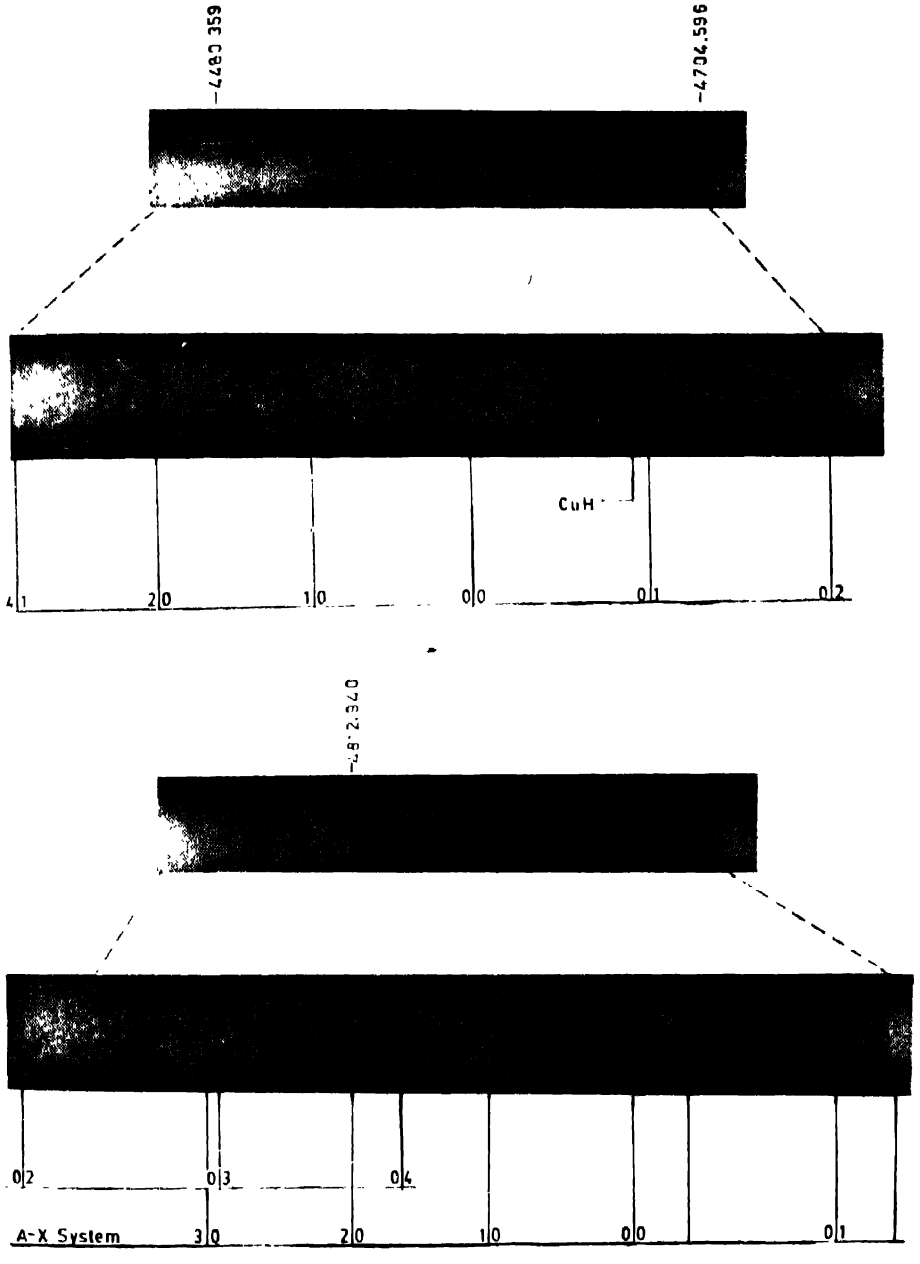

Figure 1. Thermal emission spectrum of Cu_2 molecule : B – X system (at a reciprocal linear dispersion of 7 3 Å/mm)

Plate II

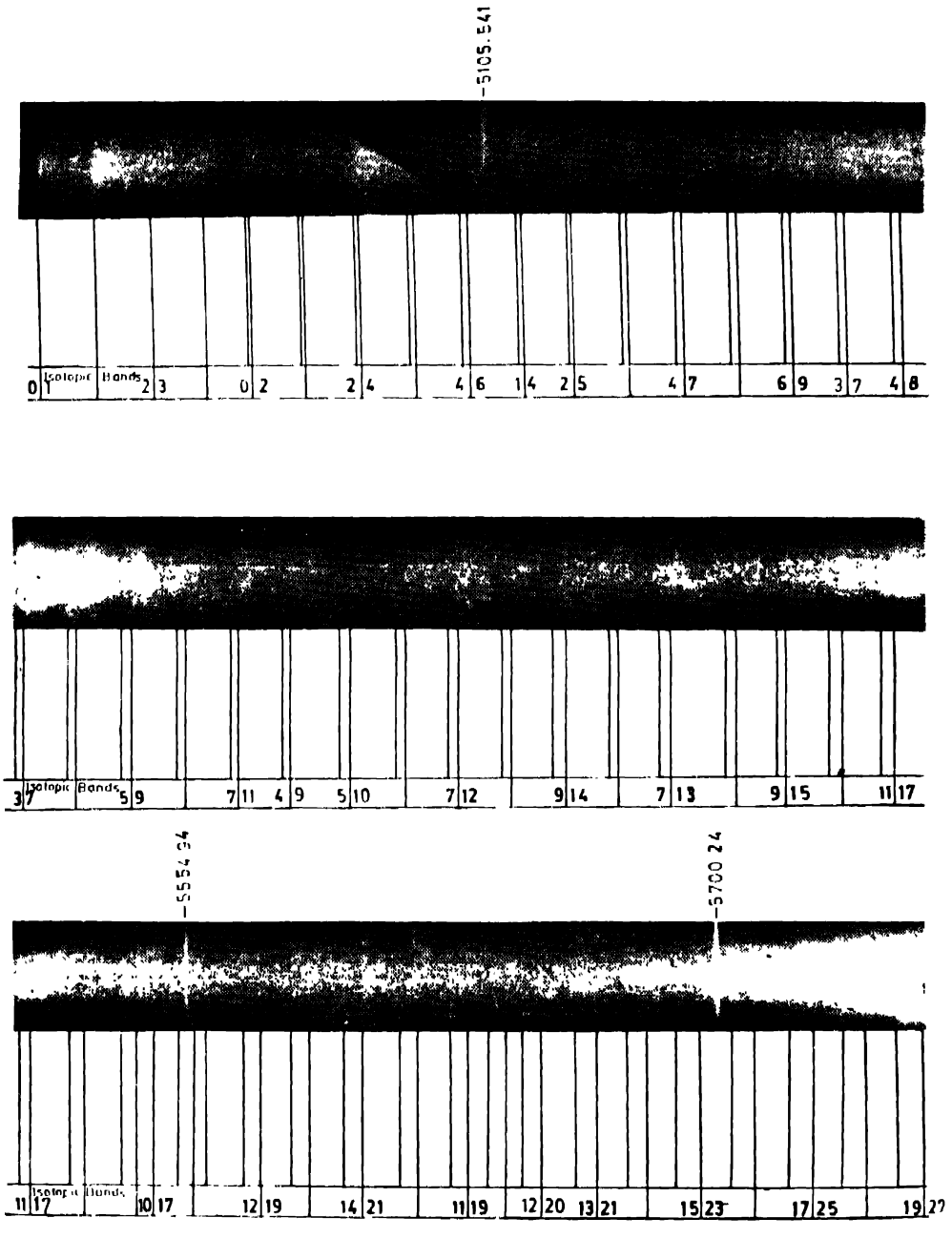

Figure 2. Thermal emission spectrum of Cu_3 molecule : A – X system (at a reciprocal linear dispersion of 7.3 Å/mm)

their vibrational classification are collected in Table 1. The analysis is confirmed by observing the isotope shifts due to ^{65}Cu in case of 92 bands.

Table 1. Additional band head data of Cu_2 molecule : A – X system

v'	v''	ν_{cal} (cm^{-1})	ν_{obs} (cm^{-1})	ν_{iobs} (cm^{-1})	Int.	v'	v''	ν_{cal} (cm^{-1})	ν_{obs} (cm^{-1})	ν_{iobs} (cm^{-1})	Int
3	0	20967 5	20967.5		2	15	21	18076 4	18075 0	18094.7	4
4	1	20892.6	20892.0		2	7	14	18209 7	18210 5	18224 3	3
5	2	20819 0	20818.5		2	8	15	18160 6	18162 6	18178 2	3
6	3	20746.8	20745 3		2	9	16	18113 0	18110 8	18128 9	4
7	4	20675.9	20675 8		2	16	23	17817 3	17815 1	17831 3	2
8	5	20606 4	20604 1		1	17	24	17780 4	17778 8	17797 6	2
2	0	20777 7	20778 1		2	18	25	17744 9	17744 7	17760.2	2
3	1	20703 5	20702 8		2	19	27	17500 1	17498.1	17516 3	2
4	2	20630.6	20632 0		2	20	28	17469 3	17468 6	17485 8	3
5	3	20559 1	20557 5		2	21	29	17440 0	17238 6	17455 8	4
6	4	20488 9	20489 2		2	22	30	17412 0	17410 8	17430 6	3
7	5	20420 1	20421 9		2	12	21	17530 0	17528 4	17550 4	2
2	2	20251 7	20249 4		3	13	22	17491 8	17493 1	17512 1	2
3	4	19923 6	19921 8	19929 1	2	14	23	17455 0	17455 3	17474 4	2
0	2	19869 9	19871.2	18874 8	4	15	24	17419 6	17421 6	17437 6	2
10	14	18766 6	18765 9	18777.1	2	16	25	17385 5	17387 5	17403 3	2
11	15	18715.5	18714 5	18726 4	2	17	26	17352 8	17351 4	17370 8	2
12	16	18665 7	18666 8	18678 0	2	18	27	17321 4	17323 1	17339 3	2
0	4	19352 1	19350.5	19358 5	6	19	28	17291 4	17289 6	17311 4	3
1	5	19287 5	19288 2	19296 1	5	10	20	17385 2	17386 5	17403 3	2
2	6	19224 2	19225 5	19234.5	5	11	21	17346 4	17347 4	17366 8	3
0	5	19096 3	19097 1	19108 0	5	12	22	17309 0	17310 2	17328 1	4
1	6	19033.7	19035.8	19045 6	6	13	23	17272 9	17273 4	17292 6	3
2	7	18972 4	18972 0	18984 3	5	14	24	17238 1	17240 2	17259 8	2
3	8	18912 5	18912 2	18921.7	5	15	25	17204 7	17203 3	17226 2	4
5	11	18553 3	18552.6	18564 7	4	16	26	17172 7	17170 5	17191 1	1
6	12	18499.5	18498.6	18512 0	2	17	27	17142 0	17143 9	17161 6	1

3.2. *System B – X :*

This system was found to lie in the region $\lambda\lambda$ 4500 – 4800 Å and was first reported by Kleman and Lindkvist [1]. They have recorded only 10 bands while authors have recorded well developed 59 bands. The bands are degraded to red and have been assigned to sequences

Δv = 3 to – 4. The sequences Δv = 3, 2, –3, and – 4 are photographed for the first time. Kleman and Lindkvist [1] have reported that spectrum recorded is diffused in this region while we have obtained a nice record. Table 2 lists band head data, visually estimated intensities and their classifications.

Table 2. Band head data of Cu_2 molecule : B – X system.

v'	v''	ν_{cal} (cm^{-1})	ν_{obs} (cm^{-1})	Int.	v'	v''	ν_{cal} (cm^{-1})	ν_{obs} (cm^{-1})	Int.
4	1	22422.9	22423 4	5*	3	4	21415.0	21416 3	3
5	2	22384.4	22384.6	3	4	5	21387 2	21386.9	3
6	3	22343.7	22345 1	2	5	6	21357.0	21358.9	3
7	4	22300.6	22301 1	2	6	7	21324.4	21326.1	3
8	5	22255.2	22255 5	2	7	8	21289.5	21290 9	2
2	0	22226 5	22226.4	7*#	8	9	21252 3	21252 7	2
3	1	22194.9	22195.3	4*#	0	2	21222.4	21221.8	5*
4	2	22160.9	22160 2	2	1	3	21203 7	21203.3	5
5	3	22124.5	22125.8	2	2	4	21182.6	21182.8	4
6	4	22085.8	22086.2	2	3	5	21159.2	21160.4	4
7	5	22044.8	22044.6	2	4	6	21133.4	21135.1	2
8	6	22001 4	22003 9	2	5	7	21105 2	21105 8	3
1	0	21989.7	21989 2	7*	6	8	21074 7	21074 7	2
2	1	21962.5	21961 1	5	7	9	21041.8	21043.1	1
3	2	21932.8	21933 6	4	8	10	21006 7	21008 1	1
4	3	21900.9	21902 1	5#	0	3	20962 5	20961 9	2
5	4	21866.6	21868 4	5#	1	4	20945 8	20946 6	3
6	5	21830.0	21831 7	3	2	5	20926 7	20925 9	2
7	6	21791.0	21792 5	4	3	6	20905 4	20906.5	2
0	0	21748.5	21748.5	7*#	4	7	20881.6	20882 2	2
1	1	21725.7	21724.5	3*#	5	8	20855.5	20857 1	2
2	2	21700.5	21701.6	5*#	6	9	20827 1	20828.9	2
3	3	21672.9	21674.8	3*#	7	10	20796 3	20796.6	2
4	4	21643.0	21643.1	3*	0	4	20704.6	20705 6	2
5	5	21610 7	21611.8	2	1	5	20690.0	20689 7	2
6	6	21576.2	21576 9	2	2	6	20673.0	20674.8	2
7	7	21539.2	21539.1	2	3	7	20653 6	20654.3	2
0	1	21484 4	21484.4	8*#	4	8	20631.9	20632.0	2
1	2	21463.7	21462 9	3#	5	9	20607.8	20609.0	1
2	3	21440.5	21441.6	2					

* Bands reported by Kleman and Lindkvist [1]

\# Bands reported by Preuss *et al* [8]

Thermal emission spectrum of Cu_2 molecule has yielded about 59 bands in the blue spectral region $\lambda\lambda$ 4400 – 4850 Å which have been explained by the proposed analysis. From the distribution of intensity in the spectrograms it is evident that the most intense bands lie on a well formed parabola as expected. In view of the above facts and results reported earlier it appears that bands have been rightly attributed due to Cu_2 molecule. The value of the ground state vibrational constants in the present systems are appeared to be identical to those obtained by Preuss *et al* [8]. A comparison between the vibrational frequencies ω_e obtained from the present vibrational analysis and an approximate values of vibrational frequencies calculated from the rotational constants B_e and D_e, using Kratzer's relation $D_e = 4B_e^3/\omega_e^2$ has been compiled in Table 3. It is clear from the table that the order of magnitude of ω_e is almost same for the various electronic states. The maximum difference between the observed and calculated bands are 2.3 cm^{-1} for the bands which are either weak or higher members of the sequence. The constants proposed by us for the different band systems are collected in Table 3.

Table 3. Spectral data of Cu_2 molecule (in cm^{-1})

System	ν_{00}	ω_e	$\omega_e x_e$	B_e	$D_e \times 10^{-8}$	ω_e^*
A	20396.0	191.9	0.348	0.10276[b]	11.34[b]	195.6
B	21748.5	245.6	2.20	0.09889[a]	6.30[a]	247.8
X		266.1	1.025	0.10874[a]	7.15[a]	268.3

* An approximate value of ω_e calculated from rotational constants

[a] Reference [8]

[b] Reference [7]

It may be recalled that as regard the system B – X all the earlier workers had attributed in to a $^1\Sigma_u^+ - \Sigma_g^+$ transition. However, there were conflicting opinions about the transitions involved in the system A – X, which was suggested as a $^1\pi_u - ^1\Sigma_g^+$ transition [4, 5] while [7] attributed it to a $^1\Sigma_u^+ - ^1\Sigma_g^+$. Recently, McCaffrey *et al* [10] and Page and Gudeman [11], on the basis of fluorescence study of Cu_2 molecule proposed that both the systems *viz*. A – X and B – X arose from the transition $^1\Sigma_u^+ - ^1\Sigma_g^+$. In the present study, we have recorded single headed and well developed bands. Thus the authors' observations are in support of the results [10,11].

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